(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 333 472 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
08.10.1997 Bulletin 1997/41

(51) Int. Cl.[6]: **C07D 311/72**, C11C 1/00

(21) Application number: **89302597.3**

(22) Date of filing: **16.03.1989**

(54) **Production of high concentration tocopherols and tocotrienols from palm oil by-products**

Herstellung von hochkonzentrierten Tocoferolen und Tocotrienolen als Nebenprodukt des Palmöls

Production de tocophénols et de tocotriénols de haute concentration à partir de produits secondaires de l'huile de palme

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

(30) Priority: **16.03.1988 AU 7273/88**
31.03.1988 AU 7565/88

(43) Date of publication of application:
20.09.1989 Bulletin 1989/38

(73) Proprietors:
- **PALM OIL RESEARCH & DEVELOPMENT BOARD**
  43000 Kajang Selangor (MY)
- **BIOINDUSTRY DEVELOPMENT CENTRE (BIDEC)**
  Minato-ku Tokyo 105 (JP)

(72) Inventors:
- **Top, Abdul Gapor MD**
  56100 Kuala Lumpur (MY)
- **Leong, Leong Wan**
  40000 Shah Alam (MY)
- **Ong, Augustine S.H.**
  Kuala Lumpur (MY)
- **Kawada, Tsukasa**
  Ministry of International Trade
  c/o Chiyoda-ku, Tokyo 100 (JP)
- **Watanabe, Hisashi**
  Ministry of International Trade
  c/o Chiyoda-ku, Tokyo 100 (JP)
- **Tsuchiya, Nozubu**
  Ministry of International Trade
  Chiyoda-ku, Tokyo 100 (JP)

(74) Representative: **Votier, Sidney David et al**
CARPMAELS & RANSFORD
43, Bloomsbury Square
London WC1A 2RA (GB)

(56) References cited:
GB-A- 2 090 836 **US-A- 4 454 329**

- **PATENT ABSTRACTS OF JAPAN, vol. 10, no. 31 (C-327)[2088], 6th February 1986; & JP-A-60 185 776 (RIKEN VITAMIN OIL K.K.) 21-09-1985**
- **PATENT ABSTRACTS OF JAPAN, vol. 10, no. 269 (C-372)[2325], 12th September 1986; & JP-A-61 93 178 (AGENCY OF IND SCIENCE & TECHNOL) 12-05-1986**

EP 0 333 472 B1

Printed by Rank Xerox (UK) Business Services
2.14.16/3.4

Description

The present invention relates to a novel method for the production of tocopherols (T) and tocotrienols (T3) from palm oil by-product much as Palm Fatty Acid Distillate (PFAD).

Tocopherols and tocotrienols are very useful substances exhibiting strong antioxidant activities and physiological activities. High concentrates of tocopherols and tocotrienols are not easily obtained by concentration of PFAD because the amounts of tocopherols and tocotrienols in PFAD are very low compared to soyabean, rapeseed and similar raw materials. PFAD is composed mainly of fatty acids, sterols, tocopherols, tocotrienols, squalene and like impurities.

Known processes for the concentration of tocopherols and tocotrienols usually use solvent extraction, solvent fractionation, ion-exchange resin treatment, etc., at the laboratory stage, but these processes are not complete or economically attractive. GB-A-2090836 describes the preparation of a tocotrienol concentrate from an oleaginous starting material by dissolving or extracting the oleaginous starting material in or with a non-polar organic solvent to form a tocotrienol-containing solution, contacting the solution with an anionic ion-exchange resin to adsorb the tocotrienols, and eluting the tocotrienols from the ion-exchange resin to give a tocotrienol-containing eluate. The Patent Abstracts of Japan, Vol. 10, No. 31 (C-327) of 6.2.86, discloses that tocopherol can be purified by steam distilling a tocopherol-containing oil sludge to remove low-boiling impurities, and purifying the residue with an aqueous solution of an alkali, followed by distillation under high vacuum, e.g. by molecular distillation. In the Patent Abstracts of Japan, Vol. 10., No. 269 (C-372) of 12.9.86 there is described a process for separating tocotrienols from the deodorised distillate fractionated in the purification process of vegetable oil or fat. This involves converting the fatty acids in the distillate to methyl esters, and subjecting the methyl esters to ion exchange chromatography.

The present invention seeks to provide a combination of unit processes which produce better quality and better yield compared to the previous proposals. PFAD relatively contains high level of tocotrienols compared with other sources and this has not been commercially exploited. It is therefore an object of the present invention to provide a novel and efficient method for the production of tocopherols and tocotrienols from PFAD.

According to one aspect of the present invention, there is provided a process for the production of tocopherols (T) and tocotrienols (T3) from palm fatty acid distillates (PFAD) which comprises:

(a) treating the PFAD with an alkyl alcohol and appropriate catalysts to convert free fatty acids and glycerides into alkyl esters by esterification and transesterification, respectively;

(b) distilling the resulting product under reduced pressure to remove a major part of the alkyl esters and leave the tocopherols, tocotrienols (T and T3) and other higher boiling point substance in the residue;

(c) cooling the residue to bring about crystallization of higher melting point substances end other impurities and filtering off the crystalline material to leave the T and T3 in the filtrate;

(d) treating the filtrate from (c) by an ion-exchange procedure with a high selectivity anionic resin to produce a concentrated T and T3 fraction;

(e) removing the solvent from the T and T3 fraction from (d) by evaporation;

(f) washing and drying the product from step (e);

(g) subjecting the product from (f) to molecular distillation to produce a further concentrated T and T3 product;

(h) deodorising the T and T3 product.

In a modified form of the above process, the PFAD is pretreated (before esterification) by distillation to remove a major part of the free fatty acids.

By optimizing the conditions for the various steps described above, it is possible to produce a product having a high concentration of tocopherols and tocotrienols with very low losses of material during the process.

A discussion of the preferred conditions for the steps described above follows:

(a) It is preferred to use p-toluenesulfonic acid, hydrochloric acid or sulphuric acid as the catalyst for conversion of free fatty acid in PFAD into alkyl esters, at temperatures between 65° and 110°C and reaction times of less than 3 hours.

Potassium hydroxide, sodium hydroxide or sodium methoxide are preferred as catalysts for conversion of glycerides into alkyl eaters at temperature between 30° and 70°C, with reaction times of 10 minutes or more.

It is also preferred to treat the reaction mixture with a chelating agent such as ascorbic acid (Vitamin C), phos-

phoric acid, maleic acid, citric acid or tartaric acid, before drying and distillation.

(b) Distillation is preferably curried out using a high heat-transfer rate falling film vacuum distillation column, operating at below 10 torr (1333 N/m^2) and at a temperature between 100° and 200°C. Under such conditions , it is possible to concentrate T and T3 from 0.5% to more than 10%, with losses of T and T3 in the distilled alkyl esters being less than 1% based on the original raw material.

(d) It is preferred to concentrate T and T3 by using an anion-exchange resin column using methanol, ethanol or hexane as the eluting solvent and an acidic solution, such as sulphuric acid or boric acid, for desorbing T and T3 from the ion-exchange resin. Concentration from an initial 8% up to 80% or more can be achieved in this manner.

(e) Solvent evaporation is preferably carried out using a falling film evaporator and a rotary short path evaporator in series operating at 50°C and 130°C respectively, and under reduced pressure which minimises denaturation of tocopherol and tocotrienols.

(g) It is preferred to carry out the molecular distillation at 140° to 220°C under a vaccum below 0.05 torr (6.7 N/m^2). A T and T3 fraction with greater than 95% concentration can then be produced from raw materials containing a 60% concentration of T and T3.

The optional pretreatment (distillation) step is preferably carried out using a high heat-transfer rate falling film distillation column at temperature between 150° and 250°C and a vacuum below 10 torr. (1333 N/m^2).

It is also preferred to minimise contact of tocopherols and tocotrienols with oxygen by nitrogen and/or nitrogen sparging throughout the various unit processes.

Process 1.

The process of the invention is further illustrated by the block flow diagram shown in Figure 1. Melted PFAD is fed into reaction vessel 5 via pipe system 1. A mixture of an alkyl alcohol and an acidic catalyst, such as p-toluenusulfonic acid (PTS) hydrochloric acid (HCl) or sulfuric acid, is introduced via pipe system 2. The reactants are heated and the esterification reaction is conducted at temperature between 65 and 110°C. Alkyl alcohol is continuously introduced into reaction vessel 5 via pipe system 4 and the evaporated alkyl alcohol is recovered and purified by the condensation and distillation set-up 6 via pipe system 3. When the reaction is completed, the reaction mixture is cooled. Another mixture of an alkyl alcohol and a catalyst, such as potassium hydroxide, sodium hydroxide or sodium methoxide, is added into reaction vessel 5 via pipe system 2 and transesterification of glycerides proceeds at temperatute between 30° and 70°C and at reaction time of 10 minutes or more. After treatment with chelating chemical such as vitamin C, phosphoric acid, maleic acid, citric acid and tartaric acid, water washing, nitrogen sparging and drying, the resulting product is passed to distillation equipment 9 via pipe system 8. Effluent is discharged via pipe system 7.

Distillation equipment 9 consists of high heat-transfer distillation column and distillate collection system. Distillation process is continuous. Alkyl esters are distilled at high vacuum at below 10 mm of Hg and at temperature between 100-200°C. Distilled alkyl esters are collected by condensation and discharged via pipe system 10 as a by-product. Retention time of T-T_3 in the distillation column is short so that deterioration is minimum. MOre than one distillation cycle may be practiced and recycling of the heavy phase is by pipe system 12. The final heavy phase of distillation equipment 9 is a mixture of T&T3 and other substances found in PFAD and is passed to crystallizer 13 via pipe system 11.

The mixture in crystallizer 13 is heated to homogeneous and then cooled to a 0-15°C in between 5-30 hours of cooling time by a programmable automatic control system. Various quantities of solvent such as acetone, ethanol and methanol, may or may not be added into the mixture in crystallizer 13 before cooling started via pipe system 14. 0.5% or more of filter aid are added into the crystallizer via pipe system 15.

The mixture in crystallizer 13 is then passed via pipe system 16 to filter 17 where the crystallized substances are retained in filter cakes. Before filtration started recycling of filtrate via pipe system 20 may be practised in order to form sufficient cake thickness on filter element 17. Positive pressure filtration is practiced either by using pump or by applying nitrogen gas via pipe system 18. The final filtrate which is basically free of higher melting point substances is passed to ion-exchange process set-up 21 via pipe system 19.

The filtrate is introduced into an ion-exchange column which consists of regenerated anion resin packing with high selectivity in adsorbing T-T3. Acidic solution such as sulfuric acid or boric acid is used to desorb T-T3 from the anion resin via pipe system 22. Solvent such as methanol, ethanol and hexane, is used for elution of the various fraction in the ion-exchange process coming from solvent recovery set-up 25 via pipe system 23. Undesirable eluted fractions or effluent are discharged for solvent recovery or for other processing via pipe system 24 and 26 respectively while the desired fractions which contain reasonable high concentration of T-T3 are passed to evaporation equipments 28 via pipe system 27.

The evaporation system 28 is designed to provide such short retention time for the T-T3 concentrate under vacuum that deterioration of T-T3 is minimum. Evaporated solvent is condensed and sent for purification via pipe system 29. The solvent tree T-T3 concentrate is passed to washing and drying equipments 31 via pipe system 30.

Water is added into a mixing vessel containing the T&T3 concentrate from evaporation equipment 28 via pipe system 32. Mixing or washing are conducted at elevated temperature under nitrogen blanket. Effluent is discharged via pipe system 33. Drying is carried out in the same or different equipment by vacuum it temperature between 90-100°C. The resulting washed and dried product is passed to molecular distillation equipment 35 via pipe system 34.

Molecular distillation is carried out at very high vacuum. High concentration of T&T3 fraction is obtained at temperature between 140-220°C and at vacuum below 0.05 torr 6.67 N/m^2. Undersirable fractions are discharged via pipe systems 36 while the high concentration T&T3 fraction is passed to deodorization equipment 38 via pipe system 37.

Deodorization is conducted at temperature between 180-250°C and at vacuum of 3-15 torr (400-2000 N/m^2). Low pressure steam is introduced into the deodorizer via pipe system 39 at a rate of 1-6% of the treated material. Distillate is collected by condenser via pipe system 40. Odourless final high concentration T&T3 is sent for consumption via pipe system 41.

All the process equipments described in above are equipped with nitrogen gas blanketing and nitrogen vacuum break systems for protecting T-T3 from oxidation.

Process 2

This process is similar to that of Process 1 except that the raw material, PFAD is pretreated by removing majority of the free fatty acid in PFAD by distillation before sending for processing by Process 1 at the same sequencing as described from (a) to (h) at Process 1.

As illustrated by the same Figure as Process 1. PFAD is passed to the storage facility of distillation equipment 9 via pipe system 42. Distillation process is continuous. Majority of the free fatty acids are distilled at high vacuum at below 10 torr (1335 N/m^2) and it temperature in between 150-250°C. Distilled fatty acids are collected by condensation and discharged via pipe system 10. More than one distillation cycle may be practiced and recycling is via pipe system 12. The final heavy phase is passed to reaction vessel 5 via pipe system 43. The processing conditions and products which flow from reaction vessel 5 onward are as described in Process 1.

Examples

Process-1

Several experiments on process-1 were conducted. Every step's conditions of example-1 and example-2 are shown in Table 1.2 - 1.9, and the results are shown in Table 2.

During methylesterification MeOH was fed continuously into the reaction vessel. And water which was by-produced during methylesterification was removed continuously for effective reaction. Acid Value decreased below 0.1 after methylesterification. Almost all glycerides which are contained in the sample (about 10%) were transesterificated with catalyst. Ascorbic acid solution was used for protection of T & T3 from denaturation. Samples were dried until the moisture was less than 0.5%

Fatty acid methylesters were removed by distillation and this treatment could achieve more than 16 folds concentration in view of T and T-T3 concentration in heavy phase as shown in Table 2.

Impurities which have higher melting points than T & T3 in the heavy phase were removed by crystallization and filtration. Crystals appeared when the samples were cooled down with or without several kinds of solvent. Crystals were removed by filtration by using the pressure of nitrogen gas.

The filtrates were loaded to regenerated anion-exchange resin in a column. Then the column was washed with 95% EtOH to purge impurities which did not attach to the ion-exchange resin. 10% of acid solution was used to desorb T & T3 from the resin. And then detached T and T-3s were collected as T and T-3 fraction by using 96% of EtOH.

Evaporations were conducted in 2 steps under the conditions described in Table 1.6. During 1st step, mainly EtOH was evaporated and in 2nd step, solvents including water were evaporated completely. After evaporation of EtOH and water, the concentrations of T and T3 were 83.2%, 87.6% respectively as shown in Table 2.

Several batches of T and T3 were mixed and water-soluble impurities could be got rid of by washing the sample twice with water, followed by drying under vacuum.

Further purification of T and T3 could be achieved by molecular distillations which were conducted in 2 steps. Firstly at lower temperature, impurities which are easily evaporated could be removed and secondly at higher temperature T and T3 could be evaporated. The impurities which show higher boiling points than T and T3 remained in the heavy phase.

Steam deodorization after molecular distillation produced final product which had no smell and was light-brown in colour.

Through our process above mentioned slight or no denaturation of T and T3 could be observed.

Process-2

Several experiments on process 2 were conducted. Every step's condition of example-3 and example-4 are shown in Tables 1.1 - 1.9, and the results are shown in Table 2. Compared to above process-1, initial stage is different. First free acids in PFAD were distilled roughly before methylesterification in order to decrease the quantity of material which is to be methylesterified. The succession of other treatments after this distillation is the same as process-1.

Table 1.1

Conditions of fatty acid distillation				
Factor	Ex-1	Ex-2	Ex-3	Ex-4
Vacuum (torr)	-	-	1.5	2.0
Temp. (c)	-	-	185	195
Time (hr)	-	-	5.0	5.0

Table 1.2

Conditions of methylesterification				
Step & Factor	Ex-1	Ex-2	Ex-3	Ex-4
Esterification				
Catalyst	$H_2SO_4$0.2%	$H_2SO_4$0.15%	$H_2SO_4$0.05%	$H_2SO_4$0.02%
Temp. (c)	90 c	95 c	90 c	95 c
Time (hr)	3	4	1.5	1.5
MeOH feed (l/h)	30	40	30	40
Transesterification				
Catalyst	Ca(OH) 0.5%	NaOH 0.4%	NaOH 0.5%	KOH 0.5%
Temp. (c)	50 c	55 c	55 c	55 c
Time (hr)	2.0	1.5	2.5	2.5
Chelator	Ascorbic-acid	Ascorbic-acid	Ascorbic-acid	Ascorbic-acid

Table 1.3

Conditions of methylester-distillation					
Factor		Ex-1	Ex-2	Ex-3	Ex-4
Vacuum	(torr)	1.5	2.0	1.0	1.0
	(N/m^2)	(200)	(267)	(133)	(133)
Temp. (c)		150	150	180	180
Time (hr)		8	10	4.5	5.0

Table 1.4

Conditions of Crystallization and filtration				
Step & Factor	Bx-1	Bx-2	Bx-3	Bx-4
Crystallization				
Solvent	EtOH 20 l	No addition	MeOH 20 l	Hexane20 l
Cooling temp. (c)	0 c	10 c	0 c	0 c
Cooling time (hr)	24	24	24	24
Filtration				
Filtration aid (%)	3.0	2.0	4.0	4.0
Filtration-pressure (kg/cm)	7	7	7	7

Table 1.5

Conditions of ion-exchange column				
Solvent	Ex-1	Ex-2	Ex-3	Ex-4
Purging	95% EtOH	95% EtOH	95% EtOH	95% EtOH
(l)	40	30	40	30
Detaching	10% Boric acid	10% Formic acid	10% Lactic acid	10% Malic acid
(l)	10	10	10	10
Elution	99% EtOH	99% EtOH	99% EtOH	99% EtOH
(l)	60	40	50	50

Table 1.6

Conditions of evaporation					
Step & Factor		Ex-1	Ex-2	Ex-3	Ex-4
1st step					
Vacuum	(N/m^2)	(2666)	(2666)	(2666)	(2666)
	(torr)	20	20	20	20
Temp. (c)		80	80	80	80
Time (hr)		4	4	4	4
2nd Step					
Vacuum	(N/m^2)	(267)	(267)	(267)	(267)
	(torr)	2	2	2	2
Temp. (c)		100	100	100	100
Time (hr)		1.5	2.0	1.5	1.5

Table 1.7

Condition of washing & drying					
Step & Factor		Ex-1	Ex-2	Ex-3	Ex-4
1st washing					
Water (l, c)		40,60	40,60	40,70	40,70
Stirring (min.)		20	20	20	20
2nd washing					
Water (l, c)		20,60	20,60	20,70	20,70
Stirring (min)		20	20	20	20
Drying					
Vacuum	(N/m^2)	(400)	(533)	(400)	(533)
	(torr)	3	4	3	4
Temp. (c)		95	95	90	100
Time (hr)		1.5	1.5	1.5	1.5

Table 1.8

Conditions of molecular distillation					
Step & Factor		Ex-1	Ex-2	Ex-3	Ex-4
1st step					
Temp. (c)		120	130	135	130
Vacuum	(torr)	0.04	0.02	0.03	0.03
	(N/m^2)	(5.33)	(2.67)	(4.0)	(4.0)
2nd step					
Temp (c)		140	170	220	200
Vacuum	(torr)	0.003	0.002	0.003	0.00
	(N/m^2)	(0.4)	(0.27)	(0.4)	

Table 1.9

Conditions of deodorization				
Factor	Ex-1	Ex-2	Ex-3	Ex-4
Temp. (c)	160	180	200	200
Vacuum (torr) (N/m^2)	2 (267)	2	2	2
Steam feed (g/hr)	500	400	300	450
Time (hr)	1.5	1.5	1.5	1.5

Table 2

The concentrations and accumulated yield of T & T3 on each step								
Step	Ex-1		Ex-2		Ex-3		Ex-4	
	Conc. (%)	Yield (%)	Conc. (%)	Yield (%)	Conc. (%)	Yield (%)	Conc. (%)	Yield (%)
MATERIAL	0.5	100	0.4	100	0.4	100	0.4	100
FA. DISTILLATION	-	-	-	-	2.1	97	2.4	98
M.ESTERIFICATION	0.5	98	0.4	99	2.1	95	2.4	94
M.E. DISTILLATION	8.2	95	10.1	96	8.4	91	9.5	90
CRYSTALLYZATION AND FILTRATION	8.3	90	10.1	92	8.4	88	9.5	88
ION-EXCHANGE AND EVAPORATION	83.2	85	87.6	80	85.1	78	93.4	78
WASHING AND DRYING	83.8	82	87.8	78	85.4	76	83.7	77
MOLECULAR DIST. DEODORIZATION	96.2	75	97.9	71	95.2	70	96.6	70

Claims

1. A process for the production of tocopherols (T) and tocotrienols (T3) from palm fatty acid distillates (PFAD) characterised in that it comprises:

   (a) treating the PFAD with an alkyl alcohol and appropriate catalysts to convert free fatty acids and glycerides into alkyl esters by esterification and transesterification, respectively;

   (b) distilling the resulting product under reduced pressure to remove a major part of the alkyl esters and leave the tocopherols, tocotrienols (T and T3) and other higher boiling point substance in the residue;

   (c) cooling the residue to bring about crystallization of higher melting point substances and other impurities and filtering off the crystalline material to leave the T and T3 in the filtrate;

   (d) treating the filtrate from (c) by an ion-exchange procedure with a high selectivity anionic resin to produce a concentrated T and T3 fraction;

   (e) removing the solvent from the T and T3 fraction from (d) by evaporation;

   (f) washing and drying the product from step (e);

   (g) subjecting the product from (f) to molecular distillation to produce a further concentrated T and T3 product;

   (h) deodorising the T and T3 product.

2. A process as claimed in Claim 1, characterised in that the PFAD is pretreated (before esterification) by distillation to remove a major part of the free fatty acids therefrom.

3. A process as claimed in Claim 1 or Claim 2, characterised in that, in step (a), p-toluenesulfonic acid, hydrochloric acid or sulphuric acid is the catalyst for conversion of free fatty acid in PFAD into alkyl esters, at temperatures between 65° and 110°C and reaction times of less than 3 hours.

4. A process as claimed in any one of Claims 1 to 3, characterised in that, in step (a), potassium hydroxide, sodium hydroxide or sodium methoxide is used as catalyst for conversion of glycerides into alkyl esters at a temperature between 30° and 70°C, with reaction times of 10 minutes or more.

5. A process as claimed in any one of Claims 1 to 4, characterised in that, in step (a), the reaction mixture is treated with a chelating agent such as ascorbic acid (Vitamin C), phosphoric acid, maleic acid, citric acid or tartaric acid, before drying and distillation.

6. A process as claimed in any one of Claims 1 to 5, characterised in that, in step (b), distillation is carried out using a high heat-transfer rite falling film vacuum distillation column, operating at below 10 torr (1333 N/m^2) and at a temperature between 100° and 200°C.

7. A process as claimed in any one of Claims 1 to 6, characterised in that, in step (d), T and T3 are concentrated by using an anion-exchange resin column using methanol, ethanol or hexane as the eluting solvent and an acidic solution for desorbing T and T3 from the ion-exchange resin.

8. A process as claimed in any one of Claims 1 to 7, characterised in that, in step (e), solvent evaporation is carried out using a falling film evaporator and a rotary short path evaporator in series operating at 50°C and 130°C respectively, and under reduced pressure.

9. A process as claimed in any one of Claims 1 to 8, characterised in that, in step (g), the molecular distillation is carried out at 140° to 220°C under a vaccum below 0.05 torr (6.7 N/m^2).

10. A process as claimed in Claim 2, characterised in that the optional pretreatment (distillation) step is carried out using a high heat-transfer rate falling film distillation column at temperature between 150° and 250°C and a vacuum below 10 torr. (1333 N/m^2).

11. A process as claimed in any one of the preceding Claims, characterised in that in order to minimise contact of tocopherols and tocotrienols with oxygen, nitrogen and/or nitrogen sparging is used throughout the various unit processes.

Patentansprüche

1. Verfahren zur Herstellung von Tocopherolen (T) und Tocotrienolen (T3) aus Palmfettsäuredestillaten (PFAD), dadurch gekennzeichnet, daß es umfaßt:

   (a) das Behandeln der PFAD mit einem Alkylalkohol und geeigneten Katalysatoren zur Umwandlung der freien Fettsäuren und Glyceride in Alkylester durch Veresterung bzw. Umesterung;

   (b) das Destillieren des resultierenden Produkts unter vermindertem Druck zur Entfernung eines Hauptteils der Alkylester unter Zurücklassung der Tocopherole, Tocotrienole (T und T3) und einer anderen Substanz mit einem höheren Siedepunkt im Rückstand;

   (c) das Abkühlen des Rückstandes, um eine Kristallisation der Substanzen mit höherem Schmelzpunkt und anderer Verunreinigungen herbeizuführen, und das Abfiltrieren des kristallinen Materials, wobei T und T3 in dem Filtrat zurückbleiben;

   (d) das Behandeln des Filtrats aus der Stufe (c) unter Anwendung eines Ionenaustauschverfahrens mit einem hochselektiven anionischen Harz unter Bildung einer konzentrierten T- und T3-Fraktion;

   (e) das Entfernen des Lösungsmittels aus der T- und T3-Fraktion aus der Stufe (d) durch Verdampfen;

   (f) das Waschen und Trocknen des Produkts aus der Stufe (e);

   (g) die Durchführung einer Molekular-Destillation mit dem Produkt aus der Stufe (f) unter Bildung eines weiter konzentrierten T- und T3-Produkts; und

   (h) das Deodorieren des T- und T3-Produkts.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die PFAD (vor der Veresterung) durch Destillation vorbehandelt werden, um einen Hauptteil der freien Fettsäuren daraus zu entfernen.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß in der Stufe (a) p-Toluolsulfonsäure, Chlorwas-

serstoffsäure oder Schwefelsäure als Katalysator verwendet wird zur Umwandlung der freien Fettsäure in den PFAD in Alkylester bei Temperaturen zwischen 65 und 110°C und Reaktionszeiten von weniger als 3 h.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß in der Stufe (a) Kaliumhydroxid, Natriumhydroxid oder Natriummethoxid als Katalysator verwendet wird zur Umwandlung von Glyceriden in Alkylester bei einer Temperatur zwischen 30 und 70°C mit Reaktionszeiten von 10 min oder mehr.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß in der Stufe (a) die Reaktionsmischung vor dem Trocknen und Destillieren mit einem Chelatbildner wie Ascorbinsäure (Vitamin C), Phosphorsäure, Maleinsäure, Citronensäure oder Weinsäure, behandelt wird.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß in der Stufe (b) die Destillation unter Verwendung einer Rieselfilm-Vakuumdestillationskolonne mit hoher Wärmeübergangsrate durchgeführt wird, die bei einem Vakuum unter 10 Torr (1333 N/m^2) und bei einer Temperatur zwischen 100 und 200°C betrieben wird.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß in der Stufe (d) T und T3 aufkonzentriert werden durch Verwendung einer Anionenaustauscherharz-Kolonne, in der Methanol, Ethanol oder Hexan als Eluierungs-Lösungsmittel und eine saure Lösung zum Desorbieren von T und T3 aus dem Ionenaustauscherharz verwendet werden.

8. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß in der Stufe (e) die Lösungsmittelverdampfung unter Verwendung eines Rieselfilm-Verdampfers und eines Kurzweg-Rotationsverdampfers, die hintereinander geschaltet sind und bei 50°C bzw. 130°C betrieben werden, unter vermindertem Druck durchgeführt wird.

9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß in der Stufe (g) die Molekulardestillation bei 140 bis 220°C unter einem Vakuum unter 0,05 Torr (6,7 N/m^2) durchgeführt wird.

10. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß die optionale Vorbehandlungs(Destillations)-Stufe durchgeführt wird unter Verwendung einer Rieselfilm-Destillationskolonne mit hoher Wärmeübergangsrate bei Temperaturen zwischen 150 und 250°C und einem Vakuum unter 10 Torr (1333 N/m^2).

11. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß zur Minimierung des Kontakts zwischen den Tocopherolen und Tocotrienolen und dem Sauerstoff während der verschiedenen Verfahrensstufen Stickstoff verwendet wird und/oder Stickstoff eingeleitet wird.

Revendications

1. Procédé pour la production de tocophérols (T) et de tocotriénols (T3) à partir de distillats d'acide gras de palme (PFAD), caractérisé en ce qu'il consiste:

   (a) à traiter le PFAD avec un alcool alkylique et des catalyseurs appropriés pour convertir les acides gras libres et les glycérides en esters alkyliques, respectivement par estérification et transestérification;
   (b) à distiller le produit résultant sous pression réduite pour éliminer une partie principale des esters alkyliques et laisser les tocophérols, les tocotriénols (T et T3) et une autre substance à point d'ébullition supérieur dans le résidu;
   (c) à refroidir le résidu pour entraîner la cristallisation des substances à point d'ébullition supérieur et d'autres impuretés et à retirer par filtration la matière cristalline pour laisser T et T3 dans le filtrat;
   (d) à traiter le filtrat provenant de (c) à l'aide d'un procédé d'échange d'ions avec une résine anionique à sélectivité élevée pour produire une fraction T et T3 concentrée;
   (e) à éliminer le solvant de la fraction T et T3 provenant de (d) par évaporation;
   (f) à laver et sécher le produit provenant de l'étape (e);
   (g) à soumettre le produit provenant de (f) à une distillation moléculaire pour produire un produit T et T3 plus concentré;
   (h) à désodoriser le produit T et T3.

2. Procédé selon la revendication 1, caractérisé en ce que le PFAD est prétraité (avant estérification) par distillation pour éliminer une partie principale des acides gras libres de celui-ci.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que, dans l'étape (a), l'acide p-toluènesulfonique, l'acide

chlorhydrique ou l'acide sulfurique est le catalyseur pour la conversion des acides gras libres dans le PFAD en esters alkyliques, à des températures comprises entre 65° et 110°C et pendant des durées réactionnelles inférieures à 3 heures.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que, dans l'étape (a), l'hydroxyde de potassium, l'hydroxyde de sodium ou le méthylate de sodium est utilisé en tant que catalyseur pour la conversion des glycérides en esters alkyliques à une température comprise entre 30° et 70°C et pendant des durées réactionnelles de 10 minutes ou plus.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que, dans l'étape (a), le mélange réactionnel est traité avec un agent chélatant tel que l'acide ascorbique (vitamine C), l'acide phosphorique, l'acide maléique, l'acide citrique ou l'acide tartrique, avant séchage et distillation.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que, dans l'étape (b), la distillation est effectuée en utilisant une colonne de distillation à film descendant et à une vitesse de transfert de chaleur élevée, fonctionnant sous un vide inférieur à 10 torr (1 333 N/m^2) et à une température comprise entre 100° et 200°C.

7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que, dans l'étape (d), T et T3 sont concentrés en utilisant une colonne de résine échangeuse d'anions en utilisant du méthanol, de l'éthanol ou de l'hexane en tant que solvant d'élution et une solution acide pour désorber T et T3 de la résine échangeuse d'ions.

8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que, dans l'étape (e), l'évaporation du solvant est effectuée en utilisant un évaporateur à film descendant et un évaporateur rotatif à chemin court fonctionnant en série, respectivement à 50°C et 130°C et sous pression réduite.

9. Procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que, dans l'étape (g), la distillation moléculaire est effectuée à une température allant de 140° à 220°C sous un vide inférieur à 0,05 torr (6,7 N/m^2).

10. Procédé selon la revendication 2, caractérisé en ce que l'étape du prétraitement éventuel (distillation) est effectuée en utilisant une colonne de distillation à film descendant, à une vitesse de transfert de chaleur élevée, à une température comprise entre 150° et 250°C et sous un vide inférieur à 10 torr (1 333 N/m^2).

11. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce qu'afin de minimiser le contact des tocophérols et des tocotriénols avec l'oxygène, on utilise de l'azote et/ou un barbotage d'azote tout au long des divers procédés unitaires.

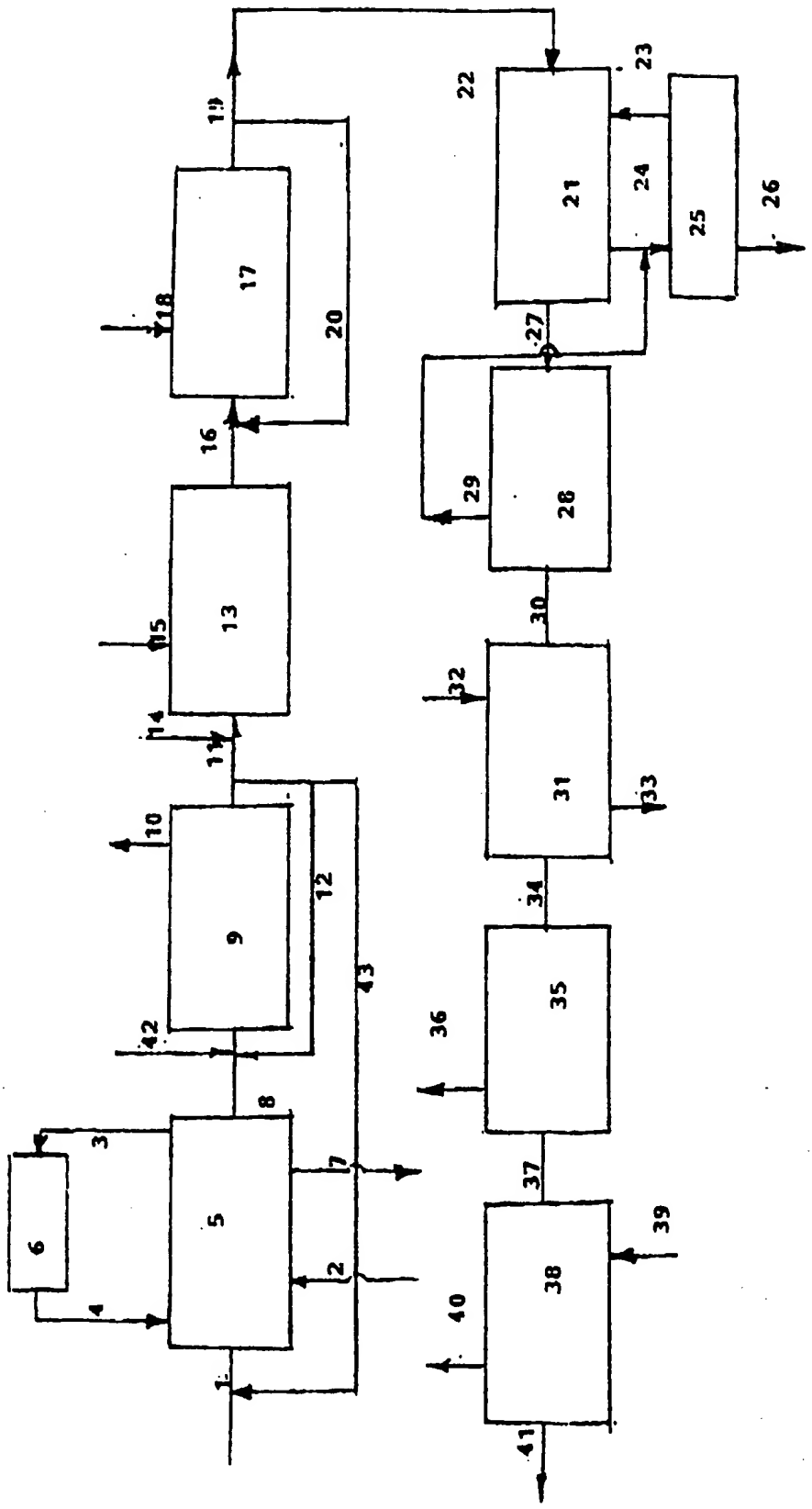
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43

Figure 1